Growth of Surface-Attached Metal-Organic Frameworks

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Introduction

- Metal-Organic frameworks (MOFs) are crystalline porous materials
- Coordination bonds between transition metal cations and organic ligands [1]
- Applications in gas separation, sensing devices and drug delivery [1]
- Film thickness, crystal orientation and homogeneity affect the functionality of MOFs
- Growing MOFs on surfaces allows to control and adjust these properties [1]
- Layer-by-layer (LbL) method used to grow surface-attached MOFs on a self-assembled monolayer (SAM)[2]

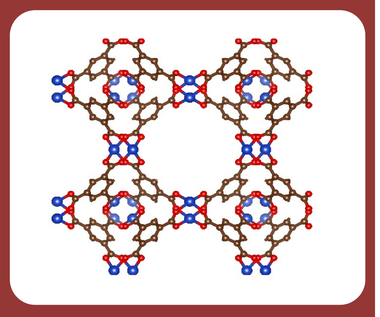


Figure 1: CuBTC structure

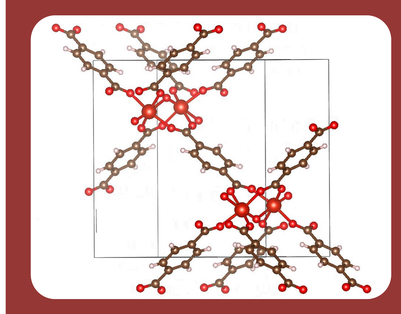


Figure 2: MIL-47 structure

- Alternating immersion of SAM into solutions of organic ligand and metal salt solution
- Thin film MOF produced [2]

Experimental

- Copper benzene-1,3,5-tricarboxylate (CuBTC) MOF was synthesized using manual LbL method at room temperature
- Gold (Au 200nm) substrate was immersed in a solution of 16-Mercaptohexadecanoic acid(16-MHDA) and ethanol for 1 hour to generate the self-assembled monolayer (SAM) with –COOH functionality.
- Layer-by-Layer method:
  - Immersion in copper acetate solution
  - Immersion in trimesic acid solution
  - Rinsing (ethanol) and drying (N_2) steps between each immersion
  - The cycle was repeated 40 times at ambient temperature

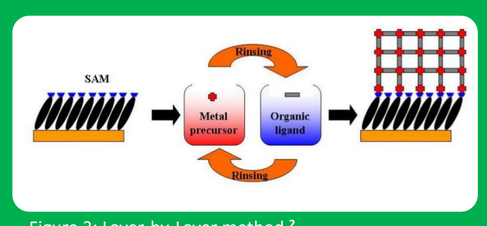
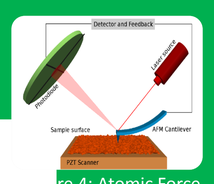


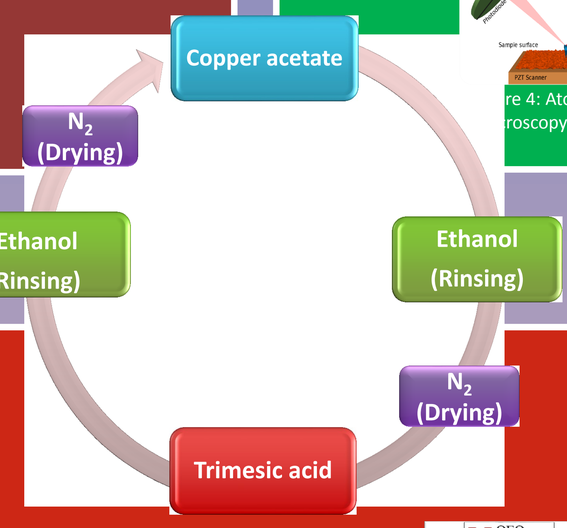
Figure 3: Layer-by-Layer method [2]

- Sample analysis by X-ray diffraction (XRD), Scanning Eelectron Microscope (SEM) and Atomic Force Microscopy (AFM)



re 4: Atomic Force roscopy principle [3]

Figure 5: SEM image of CuBTC [6]



Molecular modelling

- Grand Canonical Monte Carlo used to obtain adsorption isotherms
- Allows comparison with experimental data

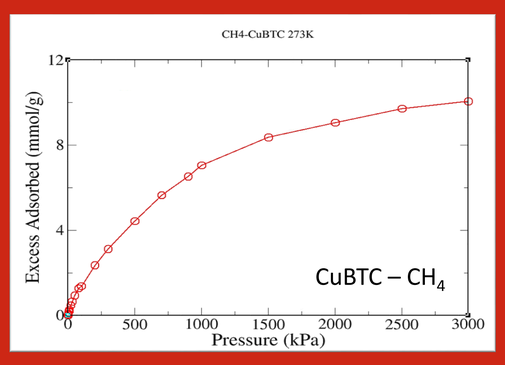
Method:

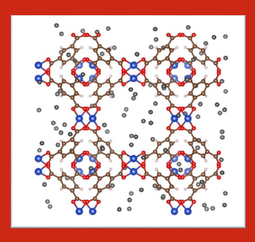
- 5.0×10^7 iterations
- 2.0×10^7 cycle equilibration period
- 3.0×10^7 cycle production run
- Lennard Jones cut-off 13 Å

- LJ parameters for MOF metal atoms were taken from UFF[3] forcefield and for non-metal atoms from DREIDNG[4] forcefield
- Partial charges and LJ parameters for the adsorbate were taken from TraPPE forcefield
- Temperature range used was 273-298K
- Adsorbates used in simulations included CH_4, H_2O and CO_2
- Point charge sets for the MOF obtained by different methods were used, these included CHELPG[6] , REPEAT [7]and QEQ[7]

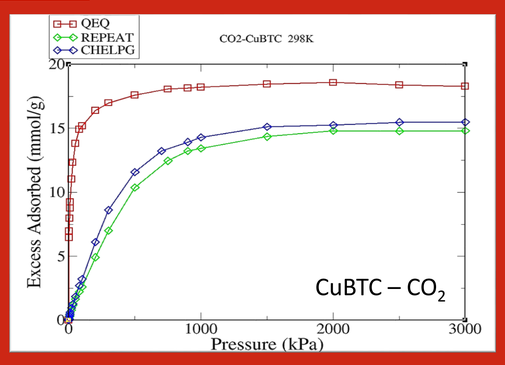
Results

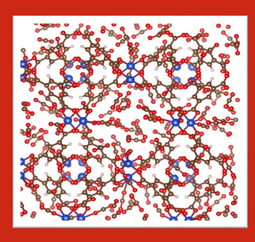
GCMC simulations



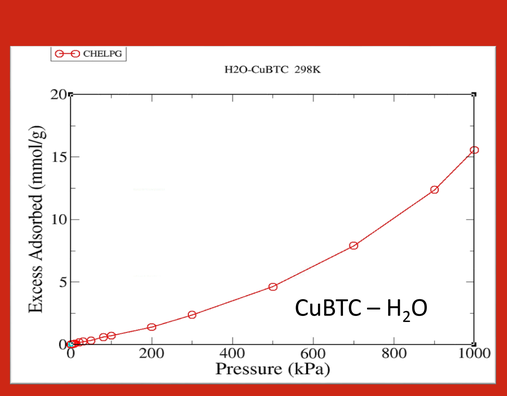


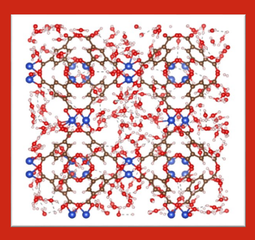
- No partial atomic charges used



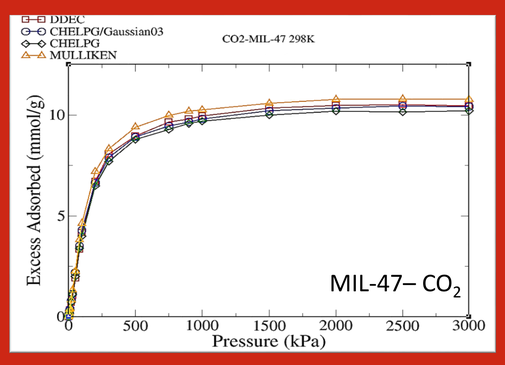


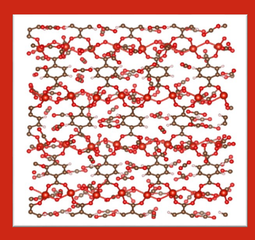
- Various partial atomic charges used for comparison
- Different isotherm shape for different charge sets





- CHELPG[6] partial atomic charges used
- Type III isotherm





- Various partial atomic charges used for comparison
- Isotherm shape remains the same for different charge sets

Conclusions

- CuBTC was synthesized using manual LbL method
- GCMC simulations indicate that partial atomic charges obtained by different methods have varying effects on different MOFs

Future work

- The experimental method will be adjusted in order to investigate the effect of factors including temperature, concentration, immersion time etc. on crystal formation and properties
- In order to establish a systematic procedure to evaluate the effect of atomic partial charges on adsorption isotherms, GCMC simulations of CuBTC and water with different sets of partial charges

References

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Acknowledgements

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